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Bio-oil production by lignocellulose fast-pyrolysis: Isolating and comparing the effects of indigenous versus external catalysts

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ABSTRACT

The effect of both indigenous (mineral components) and external (HZSM-5 zeolite) catalysts on bio-oil production by biomass fast-pyrolysis has being isolated and compared for two herbaceous and two woody biomass samples. Thereby, a variety of lignocellulosic biomasses (in both raw and de-ashed forms) have been subjected to fast-pyrolysis tests. Mineral components present in the raw biomasses were removed by an acid-washing treatment. The results obtained showed that both types of catalysts decreased the bio-oil* yield (water-free basis). However, whereas the indigenous catalysts almost did not affect the bio-oil* oxygen content, this parameter was significantly reduced when using the HZSM-5 zeolite. This finding denotes that mineral components are not really effective for bio-oil deoxygenation since they mainly promote the formation of additional char, which retains about 40% of the chemical energy contained in the raw biomass. In contrast, the external catalyst does favour oxygen removal from the bio-oil. Likewise, the deoxygenation route was strongly dependent on the type of catalyst. In the non-catalytic process dehydration was predominant, the indigenous catalysts favoured decarboxylation, whereas for the external HZSM-5 catalyst decarbonylation became the major deoxygenation pathway. Regarding the bio-oil* composition, both indigenous and external catalysts promoted the conversion of sugars and the formation of carboxylic acids, aldehydes and oxygenated aromatics. However, aromatic hydrocarbons were only produced over the external HZSM-5 catalyst, with a high proportion of alkyl-substituted benzenes and naphthalenes.

1. Introduction

Lignocellulosic biomass is a widely available and renewable resource with high potential for the production of liquid, solid and gaseous fuels [1,2]. Fast-pyrolysis, in which biomass is rapidly heated to moderate temperatures (450–550 °C), followed by a fast quenching of vapours and aerosols ($<$ 2 s of residence time) gives rise to three main product categories: solid char, non-condensable gases (H_2, CO, CO_2 and light hydrocarbons), and a dark brown liquid phase including water, with a distinct smoky odour, which is known as bio-oil. This last product may represent up to 70 wt% of the raw biomass, which renders the process highly efficient [3]. The bio-oil obtained from non-catalytic fast-pyrolysis (NCFP) consists of a complex mixture of hundreds of oxygenated species derived from the fragmentation of the three main biomass constituents. Contrary to fossil fuels, bio-oils are highly polar, dense and viscous liquids, containing typically a significant amount of water (15–30 wt%) and having acidic nature (pH of 2–3) [4]. Moreover, bio-oils are usually not miscible with hydrocarbons, which limits their direct use as fuels, which is a consequence of their chemical composition and, in particular, of its really high oxygen content (about 40 wt %), as bio-oils consist of a great variety of oxygenated functionalities, including acids, aldehydes, esters, alcohols, ethers, ketones, phenols, sugars and furans [4,5].

The quality of bio-oils can be improved by reducing the oxygen content while products are still in the vapour phase (prior to condensation), either by external (ex situ) or internal (in situ) catalytic fast-pyrolysis (CFP), depending on the placement of the catalyst bed with respect to the pyrolysis reactor [5]. Catalytic fast-pyrolysis is considered a first bio-oil upgrading step to convert this liquid product into a conventional transport fuel, something that requires almost full deoxygenation [6–9]. When pyrolysis vapours enter the pores of the catalyst they undergo a complex series of reactions, including among

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others cracking, aromatization, ketonization, aldol condensation, isomerization, oligomerization and dehydrogenation. Ideally, deoxygenation should occur mainly through decarboxylation and dehydration. In this fashion, most of the biomass chemical energy is retained in the so produced catalytic bio-oil. However, deoxygenation also takes place by decarbonylation, releasing CO, whereas additional losses of carbon and hydrogen occur due to coke formation and gaseous hydrocarbons production as a consequence of the vapours cracking [6,8,10–12].

The final composition of catalytic bio-oils is influenced by several factors, such as the catalyst type and properties, operating conditions and type of biomass. The latter has a strong influence on the quality of the obtained bio-oil, which is an aspect of high relevance considering that commercial catalytic fast-pyrolysis facilities would eventually rely on diverse feedstocks [4,13]. The determination of the char, gas, and liquid yield of different feedstocks is a very important factor for assessing the viability of biomass fast-pyrolysis. Some authors have reported in the literature that the yield of the main pyrolysis products could be predicted reasonably well from the biopolymers content of the raw biomass, according to the additivity law [14–16]. Nevertheless, according to other studies, it is not that simple as an additive law concerning the biopolymers since the interaction between the released vapours and other factors, such as ash composition [17–22], or catalyst presence [6,8,10–12,23] may also have significant effects on the final product distribution.

All biomasses contain ash-forming mineral components in the form of cations, which are bound to the organic matrix of biomass at carboxylic and/or phenolic groups, or in the form of precipitates, such as salts [24]. These indigenous minerals included in the biomass structure, such as the alkali metals potassium and sodium, and to a lesser extent the alkaline earth metals, calcium and magnesium, are known to catalyse the thermal degradation of biomass [25,26]. Alkali and alkaline earth metals (AAEM) are also known to promote secondary cracking and several thermolysis reactions that modify the pyrolysis product distribution by increasing yields of char, water, and gases [17–19,22,27] resulting in lower yield and quality of liquid organic compounds. These inorganics can be removed from biomass via various demineralization treatments [20,28,29]. Ash-removal was reported to have a major impact on the non-catalytic biomass fast-pyrolysis products, with demineralized biomasses producing more organic liquid fraction and lower char and gas products, especially CO_2. The composition of the liquid product was also significantly affected as well, with overall higher oxygen content for bio-oil produced from de-ashed feedstocks.

While a number of works in the literature has been focused on the effects derived from the removal of the mineral components for lignocellulose fast-pyrolysis, little attention has been paid in the comparison of the catalytic properties of these indigenous catalysts with those of external ones, such as zeolites. Assessing the differences and similarities between these two types of catalysis is relevant to gain further insight into the factors affecting the yield and the quality of pyrolysis bio-oils, and it can help to exploit possible synergies for the upgrading of this liquid fraction. In this context, the present work reports the results of a systematic study aimed at better understanding the effects of both indigenous (mineral components) and external (HZSM-5 zeolite) catalysts in lignocellulose fast-pyrolysis. The results obtained have been interpreted in terms of mass yield, elemental and chemical composition of the produced bio-oil, as well as taking into account the overall energy yield of this fraction with regard to the raw biomass. Remarkable differences have been found between the catalytic effects induced by these two types of catalysts on both the predominant deoxygenation pathway and their effectiveness for bio-oil upgrading. In this way, a simplified pyrolysis scheme has been proposed, illustrating the effect of both indigenous and external catalysts on the bio-oil production by lignocellulose fast-pyrolysis.

2. Experimental section

2.1. Materials

The biomass samples selected to carry out this study included forestry residues: woodchips from eucalyptus (EU) and oak (OAK); energy crops: miscanthus (MIS); and agricultural residues: straw from wheat (WS). The biomass samples were ground with a cutter mill and sieved to the desired particle size (0.5–1 mm).

To study the role of minerals on the pyrolysis performance, the biomass samples were partially de-ashed by means of a mild acid-washing pretreatment. The procedure used was as follows [29]: 50 g of the biomass were added to 1000 mL of 1 wt% HNO_3 aqueous solution and were subjected to continuous stirring at 50 °C for 2 h. After this pretreatment, the solution was vacuum filtered and the remaining biomass was washed with milli-Q water until reaching pH = 6–7. Then, the sample was dried at 105 °C for 2 days. The acid-washed samples are denoted as X-ac (X: EU, OAK, MIS and WS).

For catalytic fast-pyrolysis tests with external catalyst, HZSM-5 zeolite (Si/Al = 42) supplied by CLARIANT was employed. Prior to the pyrolysis tests, the zeolite sample was pelletized, crushed and sieved to the desired particle size of 180–250 μm.

2.2. Thermogravimetric analysis

A TGA analyser (NETZSCH STA 449) was employed to study the effect of the ash on the devolatilisation profile of the raw and acid-washed biomass samples. For that purpose, 10 mg of the sample mass were heated at 10 °C/min up to 900 °C in an Ar flow of 100 mL/min.

2.3. Pyrolysis tests

The schematic diagram of the lab-scale experimental setup used for the fast-pyrolysis experiments of raw and acid-washed biomass samples is shown in Fig. 1. It consists of a downdraft fixed-bed stainless steel reactor (16 mm i.d. and 400 mm length) heated by two electrical furnaces. The reaction temperature is measured by two type K thermocouples, placed in the pyrolysis zone and inserted into the catalyst bed, respectively. For the catalytic experiments, the reactor was loaded with 1 g of zeolite to attain a biomass/catalyst mass ratio of 5. The biomass sample (5 g) was placed in the biomass tank and kept at room temperature. A quartz wool sheet and a metallic plate were placed over the catalyst particles to avoid physical contact and possible mixing between the char particles and the catalyst bed. The pyrolysis tests were carried out at 500 °C and atmospheric pressure.

Prior to each pyrolysis experiment and during the heating of the reactor, the biomass tank and all the reaction system was purged with N_2 delivered by mass flow controllers to obtain O_2 concentration levels lower than < 0.1 vol%, ensuring that pyrolysis occurs in inert atmosphere. Once the reactor temperature reached the desired set point, the biomass was inserted in the reactor via a feeding valve and was pyrolyzed to form a solid carbonaceous residue (char) and vapours. The volatiles generated in the pyrolysis zone were swept by a N_2 flow of 100 mL/min and passed through the catalyst bed to leave rapidly the reaction zones, passing through a condensation system composed by four flasks (125 mL each) connected in series and refrigerated by an ice-water bath where the bio-oil components were condensed. Permanent gases and light hydrocarbons (C_1-C_4) were finally collected in a sampling bag.

2.4. Analytical techniques

European standards were considered for performing the proximate analysis of the biomass samples: moisture content (UNE-EN 14774-1:2010), ash content (UNE-EN 14775:2010), volatile matter (UNE-EN 15148:2010) and fixed carbon (determined by difference). In addition,

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